

A statistical model of the discotic mesophase

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Abstract. The evaluation of the thermodynamic properties of an ideal discotic mesophase needs the determination of a partition function, that depends upon two basic types of energy storage, translational and rotational. Here, we suppose we can substitute for the complex effective intermolecular potential, different mean potentials acting on each individual molecule. The defining assumptions for a discotic mesophase include the stipulations, first—that each simple disk-like molecule is, during most of the time, confined to a cell, secondly—that each molecule has an external rotation which is more or less hindered by a periodic potential. The cells are stacked in columns and the columns form a regular hexagonal array, each molecule moves in a cell as in an infinite potential well due to the neighbouring molecules.

This model has allowed the general formulation of the mesophase-free energy. From this, we obtain the form of the coefficient of isothermal compressibility when the external rotations of the molecules are hindered and the vibrational energy is weak.

Keywords. Discotic mesophase; cell theory.

1. Introduction

Some recent studies (Chandrasekhar *et al* 1977; Billard *et al* 1978; Levelut 1979) have shown that compounds with disk-like molecules can give partially ordered states; these molecules assemble in a discotic mesophase. In some ideal discotic mesophase, owing to the molecular interactions, the disks are stacked one on top of the other in columns that constitute a regular hexagonal array, and these disks remain parallel to one another.

To a first approximation, we consider that the translational, rotational motions of molecules are independent and uncoupled and their energies may be separated, and furthermore that the contribution of internal rotation is negligible.

2. Determination of the translational free energy

The examination of the mesophase leads us to think that it is possible to represent this mesophase by a model inspired by the cellular models of fluids (see Munster 1974 or Cruickshank 1971). To evaluate the translational energy of the phase, we consider that each molecule moves in a cell as in an infinite well created by the neighbouring molecules.

So we suppose that we can substitute for the complex effective intermolecular potential, different mean potentials acting on each individual molecule; and we also

suppose that the cell theory can be used to study the ideal discotic mesophase. In this theory each molecule is, during most of the time, confined to a cell whose boundaries are determined by the potential due to the neighbouring molecules. We suppose that the cells are placed between parallel planes $\Pi_1, \Pi_2, \dots, \Pi_i, \dots$. The distance d_c between two successive planes is the thickness of cells (this distance is equal to the mean distance between two successive molecules in the same column). In a column the cell centres are put in a line Δ_j , and let α be the angle between a line and the normal to plane. Between two successive planes, the cells form a regular hexagonal array.

We consider, in the bulk of fluid, a system of N cells in thermal equilibrium with the rest of fluid; let T be the temperature of the system, $V = Nv_c$, the volume (where v_c is the volume of a cell). We choose a system with N_Δ cellular strata, each of them having N_π cells ($N = N_\Delta N_\pi$). We separate the translation motion into two parts, one on a plane parallel to the planes Π_i , the other on a line parallel to the lines Δ_j .

2.1 Translation parallel to the planes Π_i

To a first approximation, we suppose that in a plane $\{\Pi_i\}$, the hexagonal cells may be replaced by circular cells of the same surface s_c (let ρ_c be the radius of these circles) and we suppose that the molecules are rigid disks. Let ρ_d be the radius of these disks and s_d their surfaces.

The average surface accessible to the centre of the molecule, the so-called free surface per molecule s_F is

$$s_F = \pi(\rho_c - \rho_d)^2,$$

because the centre of the molecule cannot approach within ρ_d of the cell's boundary.

Some geometrical considerations allow us to write

$$2\rho_c = 1.05 \delta_c$$

where δ_c is the distance between the centres of two neighbouring hexagonal cells. The canonical partition function of one of this lamellar systems may be written as:

$$Z_\pi = \left(\frac{2\pi m kT}{h^2} \right)^{N_\pi} \left\{ \frac{S_\pi}{N_\pi} \left[1 - \left(\frac{N_\pi S_d}{S_\pi} \right)^{1/2} \right]^2 \right\}^{N_\pi}$$

where $S_\pi = N_\pi s_c$ is the surface of the system.

To account for a more important disorder in a pile of molecules, we may consider that there are multiple overlaps so that each element of surface is counted more than once, let s'_c be the surface of these cells

$$s'_c = \epsilon^2 s_c \text{ or } s'_c = \eta^{-2} s_c,$$

where $\eta^{-1} = \epsilon$ and $0 < \eta \leq 1$.

It follows from this that the canonical partition function of the lamellar system is

$$Z_{\pi} = \left(\frac{2\pi m kT}{h^2} \right)^{N_{\pi}} \left\{ \epsilon^2 \frac{S_{\pi}}{N_{\pi}} \left[1 - \eta \left(\frac{N_{\pi} s_d}{S_{\pi}} \right)^{1/2} \right]^2 \right\}.$$

The free energy of the lamellar system can be obtained from the partition function, we get

$$f_{\pi} = -kT \log Z_{\pi}.$$

The system has N_{Δ} identical lamellar systems, so their contributions to the translational free energy of the system is:

$$F_{\pi} = N_{\Delta} f_{\pi}.$$

$$F_{\pi} = -N kT \log \left(\frac{2\pi m kT}{h^2} \right) - N kT \log \left\{ \frac{S_{\pi}}{N_{\pi}} \left[1 - \eta \left(\frac{N_{\pi} s_d}{S_{\pi}} \right)^{1/2} \right]^2 \right\}$$

2.2 Translation parallel to the axis Δ_j

There are N_{Δ} linear cells on a line Δ_j , these cells are considered as segments of a line, and let $d'_c = (d_c/\cos \alpha)$ be the length of a segment. We suppose that the molecules are rigid segments of the line, and let $d'_d = (d_d/\cos \alpha)$ be the length of a rigid segment where d_d is the thickness of a molecule.

The average length accessible to the centre of the molecule, the so-called free length per molecule d'_F is

$$d'_F = d'_c - d'_d.$$

The canonical partition function of one of these linear systems may be written as

$$Z_{\Delta} = \left[\left(\frac{2\pi m kT}{h^2} \right)^{1/2} \frac{1}{\cos \alpha} \frac{D_{\Delta}}{N_{\Delta}} \left(1 - \frac{N_{\Delta} d_d}{D_{\Delta}} \right) \right]^{N_{\Delta}},$$

where $D_{\Delta} = N_{\Delta} d_c$,

and the free energy of the linear system may be written as

$$f_{\Delta} = -kT \log Z_{\Delta}.$$

In the system considered, there are N_{π} identical linear systems so their contribution to the translational free energy of the system is:

$$F_{\Delta} = N_{\pi} f_{\Delta},$$

$$F_{\Delta} = -N kT \log \left[\left(\frac{2\pi m kT}{h^2} \right)^{1/2} \frac{1}{\cos \alpha} \frac{D_{\Delta}}{N_{\Delta}} \left(1 - \frac{N_{\Delta} d_d}{D_{\Delta}} \right) \right].$$

The translational free energy of a discotic mesophase is:

$$F = F_{\Delta} + F_{\pi}$$

So we see that the translational free energy of the discotic mesophase is a function of microscopic quantities which can be calculated from x-ray data (Chandrasekhar *et al* 1977; Levelut 1979).

3. Expression of rotational partition function

(i) The internal rotations in the molecule originate essentially from the flexibility of the lateral chains; so their contributions to the free energy of the mesophase is negligible to a first approximation (the moments of inertia of these lateral chains are very small compared with the moment of inertia of the molecule).

(ii) Now, we consider the rotation of the molecule as a whole; the central part of the molecule is a rigid body but the lateral chains are flexible. The rigid part of the molecule has an axis of symmetry δ_R of order 3 which passes through the centre of mass and is perpendicular to the plane of the molecule. On account of the flexibility of the lateral chains, the moment of inertia of the molecule does not have a constant value. Yet, to the first approximation, we can replace real molecules by mean molecules with lateral chains in fixed mean positions. Then the molecule as a whole and the rigid part of the real molecule have the same symmetry. Let J be the moment of inertia of this mean molecule.

The rotation of a molecule as a whole is more or less hindered by the presence of lateral chains, both its own and those of others. According to the physical conditions, the distance between the centres of neighbouring molecules is more or less important. It is evident that if this distance is larger than the diameter of a molecule when it reaches its full size, the interactions of the lateral chains are weak and consequently the rotation of the molecule as a whole is little hindered but it is evident that if this distance is smaller than the diameter of this full-sized molecule then the rotation is more hindered or forbidden. Moreover the interactions of the lateral chains depend on the positions of the molecules in the nearest cells; so interactions exist between the translational and rotational degrees of freedom of the neighbouring molecules that we do not take into account.

To a first approximation, these interactions of the lateral chains may be approximated by the following sinusoidal potential

$$U = \frac{U_0}{2} [1 - \cos \sigma \phi],$$

where ϕ is the rotation of the molecule. $\sigma=6$ for the molecule of benzene-hexa-*n*-alkanoates (Chandrasekhar *et al* 1977) and $\sigma=3$ for the molecule of hexa alkoxyderivatives of the triphenylene (Billard *et al* 1978). It is evident that the value of U_0 depends on V/N and T .

From this approximation, it follows that the wave equation may be written as

$$\frac{d^2\psi}{d\phi^2} + \frac{8\pi^2J}{h^2} \left[E - \frac{U_0}{2}(1 - \cos \sigma \phi) \right] \psi = 0,$$

(see, for example Munster 1974 or Pacault 1963).

This equation gives us

$$\frac{d^2\psi}{dx^2} + (a + 2q \cos 2x) \psi(x) = 0$$

which is the Mathieu equation (see for example Wittacker and Watson 1973) where

$$q = \frac{8\pi^2JU_0}{\sigma^2 h^2}, \quad a = \frac{32\pi^2J}{\sigma^2 h^2} \left[E - \frac{U_0}{2} \right] \text{ and } x = \frac{\sigma}{2} \phi.$$

There is an infinite sequence of discrete energy levels which are not degenerate.

It follows that the hindered rotational partition function is:

$$\mathcal{Z}_R = (Z_R)^N$$

where
$$Z_R = \sum_i \exp -\frac{E_i}{kT}.$$

When the external rotations of the molecule are forbidden,

$$U_0 \gg kT,$$

and we may expand the approximate potential in a series and retain only the first term in this series, we obtain

$$U = \frac{U_0}{2} \left[\frac{1}{2} \sigma \phi \right]^2,$$

which is a potential of a simple harmonic oscillator.

Then the partition function Z_R becomes a vibrational partition function.

Of course, in the two cases, the quantity U depends on the sizes of cells and of molecules. So the value of Z_R depends on T and on V/N as well. As for the weak vibrations, the correspondent free energy is negligible. We determine, in these conditions, some thermodynamic properties of the mesophase.

4. Some thermodynamic properties of the discotic mesophase

We restrict our study to the effects of the lamellar or linear strains which produce a variation of the size of the cells but do not change the shape of the cells.

4.1 General study

We suppose that lamellar stress acting on the regular hexagonal array is

$$t_\pi = - \left(\frac{\partial f_\pi (N_\pi, S_\pi, T)}{\partial S_\pi} \right)_{N_\pi, T}$$

then
$$t_\pi = \frac{N_\pi kT}{S_\pi} \left[1 - \eta \left(\frac{N_\pi s_d}{S_\pi} \right)^{1/2} \right]^{-1},$$

and the linear stress acting on the columns is:

$$t_\Delta = - \left(\frac{\partial f_\Delta (N_\Delta, D_\Delta, T)}{\partial D_\Delta} \right)_{N_\Delta, T},$$

then
$$t_\Delta = \frac{N_\Delta kT}{D_\Delta} \left(1 - \frac{N_\Delta d_d}{D_\Delta} \right)^{-1}.$$

From this, it follows that the translational and rotational specific heat and the coefficients of thermal expansion α and the isothermal compressibility κ may be determined. The application of this model to the study of the coefficient of isothermal compressibility presents some particularities, therefore we chose this study, to set an example.

In this model, we suppose that the translations parallel to the axes Δ and the translations parallel to the planes Π are independent and uncoupled, so it is not possible to consider the strains caused in the planes Π by stresses parallel to the axes Δ and vice versa. So, it is necessary to consider only particular stresses when studying the isothermal compressibility of the ideal discotic mesophase.

(i) When the ideal mesomorphic phase is exposed to homogeneous lamellar stresses t_π , the (lamellar) coefficient of isothermal compressibility may be written:

$$\begin{aligned} \kappa_\pi^{-1} &= - S_\pi \left[\frac{\partial t_\pi}{\partial S_\pi} \right]_{N_\pi, T} \\ &= + \frac{N_\pi kT}{S_\pi} \left\{ \frac{1 - \frac{1}{2} \eta \left[\frac{N_\pi s_d}{S_\pi} \right]^{1/2}}{\left[1 - \eta \left[\frac{N_\pi s_d}{S_\pi} \right]^{1/2} \right]^2} \right\}. \end{aligned}$$

(ii) When the ideal mesomorphic phase is exposed to uniform linear stresses t_Δ , the (linear) coefficient of isothermal compressibility may be written:

$$\begin{aligned} \kappa_\Delta^{-1} &= - D_\Delta \left(\frac{\partial t_\Delta}{\partial D_\Delta} \right)_{N_\Delta, T}, \\ &= + \frac{N_\Delta kT}{D_\Delta} \left[1 - \frac{N_\Delta d_d}{D_\Delta} \right]^{-2}. \end{aligned}$$

The signs of lamellar and linear stresses have been chosen arbitrarily. From this choice, it follows that the lamellar and linear coefficients κ_π and κ_Δ are positive. Nevertheless, as in the case of graphite, it is possible for the coefficient κ_Δ to be positive and coefficient κ_π to be negative (Riley 1945) (indeed the graphite, as the discotic mesophase, has a lamellar structure) then it would be necessary to write:

$$t_\pi = + \left(\frac{\partial f_\pi}{\partial S_\pi} \right)_{N_\pi, T}$$

4.2 Coefficients of isothermal compressibility for two hexa-alcoxy derivatives of the triphenylene

An actual calculation of the coefficients κ_π and κ_Δ is now possible. For example, we propose to calculate the isothermal compressibilities at 85°C of two hexa *n*-alcoxy-2-3-6-7-10-11 derivatives of the triphenylene, the lateral straight chains of which are alkanes with 5 or 7 carbon atoms (Billard *et al* 1978; Levelut 1979).

The mean distance d_c between two successive molecules in the same column is 3.59 Å for the two compounds, and the thickness d_d of the molecules can be chosen between 1 Å and 1.5 Å, so the coefficient κ_Δ is between 0.5 10¹¹ and 0.4 10¹¹ N⁻¹. The distance δ_c between the centres of two neighbouring hexagonal cells is 18.94 Å for the pentyl derivative and 21.94 Å for the heptyl derivative. If we suppose that the radius of the disk which represents the molecule is equal to the radius of central part of this molecule, which is not realistic, we have $\rho_d = 5.02$ Å for the two compounds. But some other values of ρ_d can be chosen; it is possible, for example, to choose this radius equal to the distance between the centre of the molecule and one of the carbon atoms of the lateral straight chains, when the molecule is fully extended.

Table 1 gives the calculated values of κ_π . In this table, for the two derivatives, the values of ρ_d are equal to the distances between the centre of the molecule and the antepenultimate, penultimate and last carbon atoms of the lateral chains. A pressure $p = t_\Delta s_c^{-1}$ corresponds to the linear stress t_Δ and a pressure $p = t_\pi d_c^{-1}$, to the lamellar stress t_π ; as a result, it is possible to make a comparison between the

Table 1. $\kappa_\pi N^{-1} m$ for two hexa alcoxy-derivatives of the triphenylene at 85°C

ρ_d Å	pentyl derivative ($\rho_c = 9.94$ Å)		heptyl derivative ($\rho_c = 11.52$ Å)	
	$\eta = 0.9$	$\eta = 1$	$\eta = 0.9$	$\eta = 1$
5.02	237	204	380	335
7.8	155	51	—	—
9.35	25	4	—	—
10.3	5	no sense	54	18
11.7	—	—	11	no sense
12.7	—	—	0.01	no sense
			(not very significant value)	

coefficients $\kappa_{\Delta} s_c$ and $\kappa_{\pi} d_c$ and the usual coefficient of isothermal compressibility, κ .

Table 2 gives the calculated values of coefficients $\kappa_{\Delta} s_c$ and $\kappa_{\pi} d_c$ for two hexa-alcoxy derivatives of the triphenylene.

At present, we can only note that the values of these coefficients and the experimental values of the coefficients of isothermal compressibility for some compounds closely related to studied compounds are in the same region; so $\kappa = 5 \cdot 10^{-10} \text{ N}^{-1} \text{ m}^2$ for para azoxy anisole (Chin and Neff 1975) and $\kappa = 5, 7 \cdot 10^{-10} \text{ N}^{-1} \text{ m}^2$ for *N*-(*p* ethoxy benzylidene) *p*-*n* butyl aniline (Kuss 1978). We note that the coefficient κ_{Δ} is linked to the relative change of the average distance d_c between the neighbouring molecules in the column for a change Δt_{Δ} of linear stresses exerted on the ideal discotic mesophase

$$\kappa_{\Delta} = -\frac{1}{d_c} \left[\frac{\Delta d_c}{\Delta t_{\Delta}} \right]_T,$$

and that the coefficient κ_{π} is linked to the relative change of the distance δ_c between the centres of two neighbouring hexagonal cells for a change Δt_{π} of lamellar stresses exerted on the ideal discotic mesophase

$$\kappa_{\pi} = -2 \frac{1}{\rho_c} \left[\frac{\Delta \rho_c}{\Delta t_{\pi}} \right]_T = -2 \frac{1}{\delta_c} \left[\frac{\Delta \delta_c}{\Delta t_{\pi}} \right]_T.$$

5. Conclusion

From the structure of a discotic mesophase, we have built up a model inspired by the cell theory of liquids to determine translational free energy of the mesophase.

From this cellular model, it is possible to determine the thermoelastic coefficient of the mesophase as a function of the size of the molecule and of the mean distance

Table 2. $\text{K} \cdot 10^{10} \text{ N}^{-1} \text{ m}^2$ ($\text{K} \cdot 10^{11} \text{ dyne}^{-1} \cdot \text{cm}^2$)

\AA	pentyl derivative		heptyl derivative		
$\kappa_{\Delta} s_c$	d_d				
1		15		21	
1.5		12		17	
$\kappa_{\pi} d_c$	ρ_d	$\eta = 0.9$	$\eta = 1$	$\eta = 0.9$	$\eta = 1$
	5.02	850	732	1364	1203
	7.8	556	183	—	—
	9.35	90	14	—	—
	10.3	18	no sense	194	65
	11.7	—	—	39	no sense
	12.7	—	—	0.04	no sense
				(not very significant value)	

between the neighbouring molecules, these microscopic quantities may be determined by x-ray studies.

It is still too soon to judge the appropriateness of this model to account for the thermodynamic properties of the discotic mesophase. Nevertheless it seems quite obvious that a cellular model is more closely related to the real system when this system is a discotic mesophase than when it is a liquid.

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